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Effect of Thermal Exposure on the Properties of Phenolic Composites: Dynamic Mechanical Analysis

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ABSTRACT: Changes in the dynamic response of glass-reinforced phenolic composites following thermal exposure at 180°C for periods of time up to 28 days were monitored using dynamic mechanical analysis. Four phenolic resins were investigated: a resol/novolac blend, a phenolic–furan novolac/resol graft copolymer, a novolac, and a resol. Reactive blending and copolymerization of phenolic resins are currently being investigated to determine if these techniques will produce phenolic resins (and composites) that have improved impact properties and retain the excellent high-temperature properties of resol and novolac phenolic resins. The results indicate that thermal aging at 180°C for 1 day led to a more complete cure of all four phenolic resins as indicated by an increase in the temperature of the maximum of plots of both loss modulus (E'') and tan δ versus temperature. The storage modulus (E') of the composites at 40°C varied little following thermal aging at 180°C for 1 day but decreased with increasing exposure time for samples aged 2, 7, and 28 days. Thermal aging led to an increase in E' at higher temperatures and the magnitude of E' at a given temperature decreased with increasing exposure time. The magnitude of E'' and tan δ decreased with aging time for all resins, although E'' and tan δ were larger for the blend and copolymer composites than for the novolac and resol composites. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 385–395, 2001

Key words: phenolic; composite; dynamic mechanical analysis; cure

INTRODUCTION

In recent years, there has been a growing interest in the use of composite materials for the manufacture of structural components in the shipbuilding industry. This is the result of a number of properties that make composites attractive alternatives to more traditional structural materials. These properties include high specific strength and modulus, corrosion resistance, good fatigue and fracture properties, relative ease of fabrication into complex shapes, and ease of repair offered by composite materials. In particular, the high specific strength and modulus of composites provide an opportunity for real reductions in the topside weight of ships, and the resistance of polymeric resins to the marine environment could substantially reduce costs associated with the corrosion of metal components.

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The widespread use of composite materials on board ships has been slowed by concerns over their fire resistance. One approach to improving the fire resistance of composites has been to add fire retardants and smoke suppressants to the resin. A drawback to this approach is that the additives may cause a degradation in the mechanical properties of the resin and, therefore, the composite. Another is that flame retardants, designed to raise ignition temperature and reduce flame spread of a resin, may increase the release of smoke and toxic gases from the resin once the fire is underway.

A second approach to improving the fire performance of composites is through the use of resins that are less susceptible to heat and flame. The phenolic resins are a class of compounds that have superior fire and flammability properties compared to other thermoset resins such as the polyesters and epoxies. These properties are inherent to phenolics and are directly related to the structure and thermal degradation mechanism of these polymers. The thermal degradation of phenolic resins leads to the production of char that results in extremely low flame-spread rates compared to flame-retardant polyester resins. Phenolics have a very high critical oxygen index (45–70%) and therefore are difficult to ignite and maintain in a burning condition.[1] Phenolics are also among the lowest smoke-producing plastics known. In addition, phenolics produce smoke that has lower toxicity than that of most flame-retardant plastics. For instance, compared to a flame-retardant polyester resin, a standard phenolic resin produced four times less carbon monoxide, six times less hydrogen chloride, and levels of hydrogen bromide an order of magnitude lower.[2]

Phenolic resins are produced by a condensation reaction between phenol and formaldehyde. Phenolics are divided into two broad classes: resols and novolacs. Resols are often referred to as one-step resins since they can be cured by heat alone and require no crosslinking agent. These resins are formed by reacting phenol with an excess of formaldehyde under alkaline conditions. Typical ratios of formaldehyde to phenol used in the preparation of resol resins are between 1.5:1.0 and 3.0:1.0. The mechanisms of the reactions leading to the formation of resol phenolic resins have been the object of a number of studies. The formation of hydroxymethylphenols,[3,4] the condensation reactions of hydroxymethylphenols to form resol precursors,[5,6] and the effect of pH and temperature on these reactions[7,8] have received considerable attention. The chemistry is difficult to study as the result of the intractable nature of the cured resin. However, the evidence suggests that methylene linkages predominate (see Fig. 1) although the cured resin may have a number of different crosslinks.[9]

Novolacs are prepared by reacting an excess of phenol with formaldehyde under acidic conditions. A typical ratio of phenol to formaldehyde is 1.25:1.00. Unlike resols, novolacs require the addition of a crosslinking agent and heat to achieve cure. Hexamethylenetetramine (HMTA), a common crosslinking agent, is added at levels between 8 and 15%.

Methylene linkages also predominate in cured novolac phenolic resins (see Fig. 2).[9] However, when HMTA is used as a crosslinking agent, there are a small number of nitrogen-containing crosslinks. Model studies have identified benzylamines, benzoxazines, and azomethines as intermediates in an HMTA-based cure reaction of novolac phenolics.[10,11] The rate of formation of benzylamines has been shown to depend on the presence of water, free phenol, and lower pH.[10] Crosslinking results in the release of ammonia but the cured resin may still contain up to 6% bound nitrogen.[5] The rate of cure of novolac resins has also been shown to depend on the structure of the novolac; 2,2-′-substituted (high *ortho*) phenol-based novolacs cure more rapidly than do 2,4-substituted phenol-based novolacs.[12]

Phenolics also exhibit good retention of both strength and modulus and have excellent creep resistance at higher temperatures. The thermomechanical properties are directly related to the high crosslink density that results from cure of these resins. Dynamic mechanical analysis (DMA) was used to follow changes in the structure of phenolic resins that result from cure of these resins.[13,14] Crosslinking has been found to result in an increase in the glass transition temperature (T_g) of the polymer, an increase in the storage modulus (E') of the polymer at a given temperature, and a decrease in the damping or loss factor (tan δ) of the polymer.

However, high crosslink density also results in relatively low strain-to-failure, generally in the range from 0.4 to 0.8%,[15] and, therefore, plastics that are relatively brittle. This has led to concern about the use of phenolics in applications where shock loads are anticipated. One approach to improving the impact strength of phenolics has been the use of short reinforcing fibers. Fibers have produced improvements in the impact resistance

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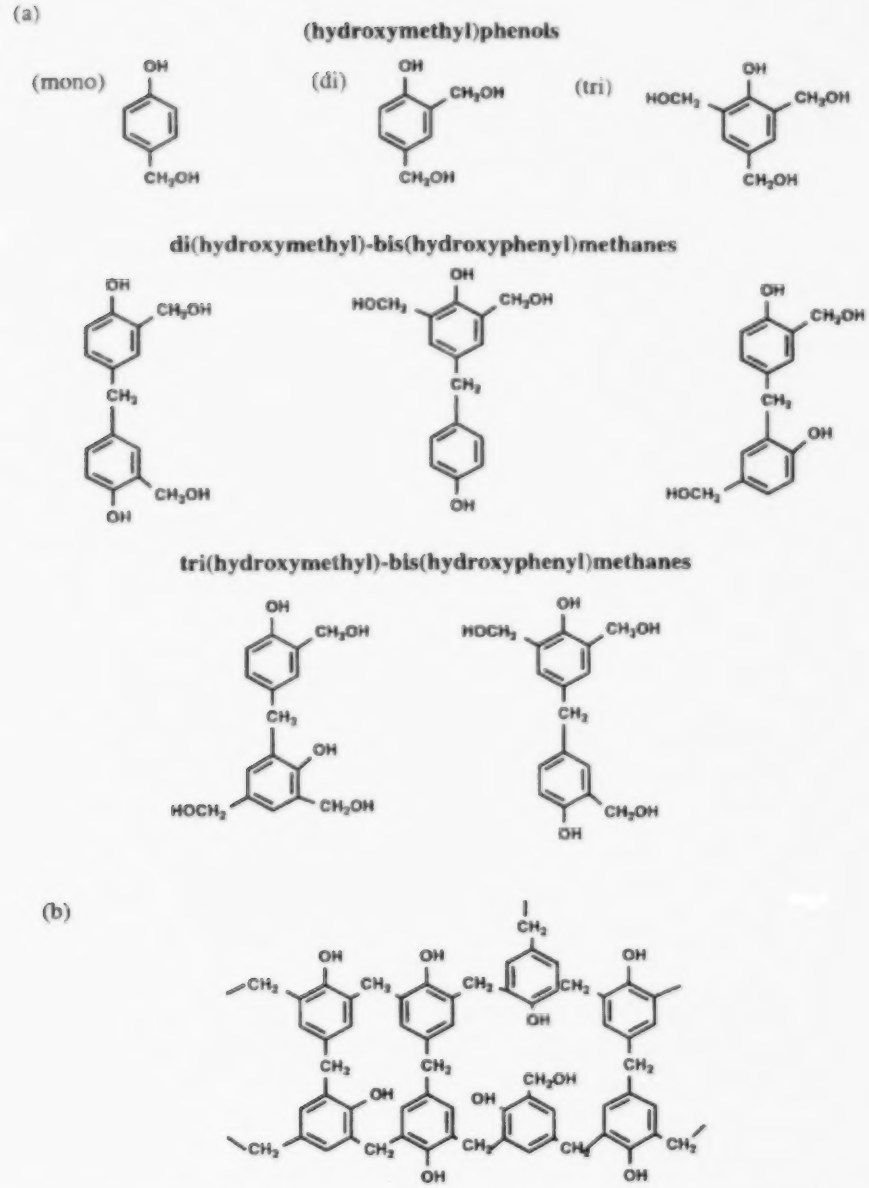

Figure 1 (a) Resol phenolic resin precursors: structures of some typical mono-, di-, and tri-(hydroxymethyl)phenols and di- and tri(hydroxymethyl)-bis-(hydroxyphenyl)-methanes; (b) structure of a cured resol phenolic resin.

of phenolics to the point where impact strengths are similar to those of some reinforced thermoplastics.[16]

Another approach to improving the impact strength of phenolics is to modify the structure and therefore the response of the phenolic to a

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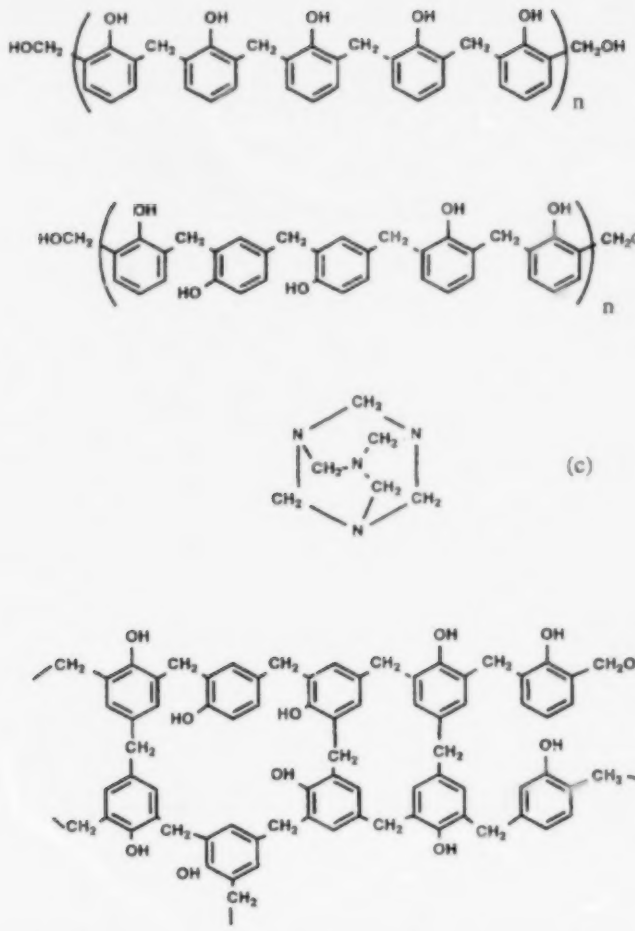

Figure 2 Novolac phenolic resin uncrosslinked polymers. high-*ortho* polymer, (b) novolac phenolic resin uncrosslinked polymers: polymer with *ortho* and *para* linkages. (c) HMTA; (d) structure of a cured novolac resin.

shock load. In this article, the changes in the dynamic mechanical response of modified phenolic resin composites following thermal aging at 180°C for periods of time up to 28 days are compared to changes in standard resol and novolac resin composites. The modified resins were a resol/novolac blend and a furan novolac resol graft copolymer. The changes in the dynamic mechanical response are discussed with respect to changes in the structure of the composites, such as increased crosslinking, changes at the fiber–resin interface, and degradation resulting from thermal exposure.

EXPERIMENTAL

Materials

Resins

The four phenolic resins used in the study were supplied by Plastics Engineering Co. (Sheboygan, WI). They were a resol phenolic (Plenco 11956), a novolac phenolic (Plenco 21483), a 70/30 blend of the resol and novolac resins, and a phenolic–furan novolac and resol graft copolymer.

The resol phenolic had a formaldehyde:phenol ratio of 1.266:1.0, a number-average molecular

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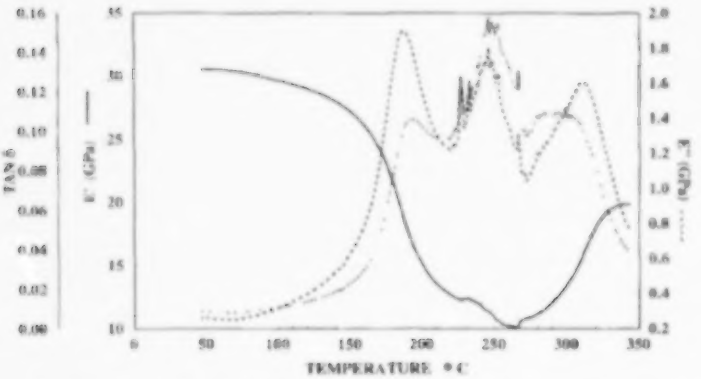

Figure 3 Storage modulus (E'), loss modulus (E''), and tan δ versus temperature for a sample of novolac/S-glass composite (as manufactured).

weight of 139, and a weight-average molecular weight of 173. The novolac resin had a number-average molecular weight of approximately 1000 and a weight-average molecular weight of approximately 15,000. It was cured with 10% HMTA.

The 70% resol/30% novolac blend contained the resol precursors shown in Figure 1 and the novolac resin precursor shown in Figure 2. No HMTA was added to the blend prior to curing. However, the *ortho* and *para* positions of the novolac are active with respect to the methylol groups of the resol resin and would be positions where crosslinking could take place during the cure of the blend. This blend exhibited a single glass transition temperature, indicating that the two resins were miscible.

The phenolic–furan novolac resin used in the copolymer had a number-average molecular weight of approximately 600 and a weight-average molecular weight of approximately 2000. The copolymer was formed by grafting this novolac to the Plenco 11956 resol phenolic resin. No HMTA was added to the phenolic–furan novolac/resol graft copolymer to promote crosslinking in this resin. As was the case with the resol/novolac blend, the *ortho* and *para* positions of the novolac resin were active with respect to the methylol groups of the resol portion of the resin. Crosslinking at these sites would lead to the cure of the copolymer. The production of all these resins was described before by the authors.[17]

Composites

The S-glass mats (Hexcel 4533-60-F-72, Seguin, TX) and E-glass mats (Hexcel 7533-60-S-72, Seguin, TX) were treated with a silane-based coupling agent (Dow Corning Z-6020 coupling agent, Midland, MI). The resins were combined with methanol (10%) and blended in a high-speed mixer prior to application to the glass-fiber mats. The resin-impregnated mats were heated to 90°C for 45 min and 17 mats were stacked (0/90) and molded at 145°C using a pressure of 4.9 MPa. The molded composite sheets were approximately 1/8-in. thick.

Thermal Aging

Thermal aging of the phenolic composites was carried out in an oven at 180°C. Samples were aged for 1, 2, 7, and 28 days prior to DMA.

Storage Modulus (E'), Loss Modulus (E''), and Tan Δ

DMA was carried out on a DuPont Model 9300 DMA in the fixed-frequency mode at 2 Hz. A heating rate of 10°C/min was used for all analyses. The glass transition temperature was taken as the maximum in the plot of either E'' or tan δ versus temperature, where tan δ is the ratio of the loss modulus (E'') to the storage modulus (E').

RESULTS AND DISCUSSION

DMA

Plots of the storage modulus (E'), loss modulus (E''), and tan δ versus temperature (T) for a sample of the S-glass reinforced novolac phenolic composite are shown in Figure 3. The magnitude of E'

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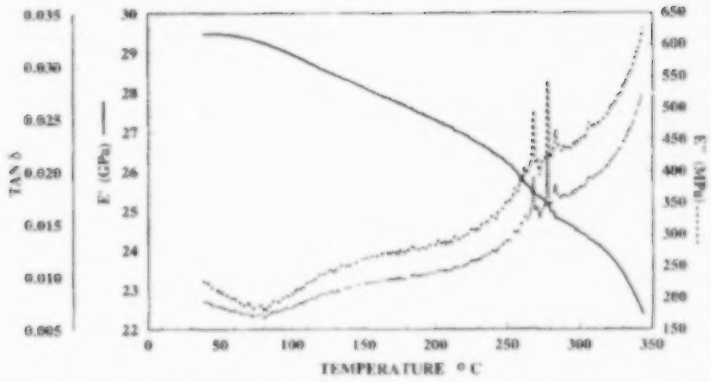

Figure 4 Storage modulus (E'), loss modulus (E''), and tan δ versus temperature for a sample of novolac/S-glass composite aged at 180°C for 1 day.

decreased rapidly between 150 and 200°C, from approximately 30 GPa to less than 12 GPa, while E'' and tan δ went through maxima at 187 and 192°C, respectively. The rapid decrease in E' between 150 and 200°C and the maxima in the plots of E'' and tan δ versus temperature are characteristic of the glass transition of the resin.[13] It is interesting to note that E' began to increase as the sample was heated above 250°C. This was attributed to the low degree of cure of the novolac resin during molding.[14] As the sample is heated, E' drops rapidly at the glass transition. The cure of the resin continues as the temperature is increased, which results in an increase in E'.

Plots of E', E'', and tan δ versus T for the same composite following thermal aging at 180°C for 1 day are shown in Figure 4. A comparison of Figures 3 and 4 indicates that the dynamic mechanical response of the composite changed dramatically following thermal aging. There was no abrupt decrease in the magnitude of E' when the thermally aged sample was heated from 40 to 350°C, that is, E' gradually decreased with temperature, from approximately 30 to 22 GPa, over the entire temperature range of the DMA run. The plots of E'' and tan δ versus T did not go through a maximum but increased as the temperature was increased from 40 to 350°C. In addition, the magnitudes of E'' and tan δ at a given temperature were much lower than for the unaged sample.

The higher storage modulus at elevated temperatures and the decrease in tan δ are consistent with postcuring of the novolac resin. It is interesting that the initial storage modulus of the composite aged for 1 day at 180°C is lower than that for the unaged composite. It has previously been observed that the initial storage modulus of a novolac composite decreased with increase in the cure temperature.[14] It was determined that this resulted from a decrease in the density of samples cured at higher temperatures.[14]

Storage Modulus (E')

The initial storage moduli (E_i'), that is, E' at ambient temperature, of the four phenolic composites after 0, 1, 2, 7, and 28 days of aging at 180°C are listed in Table I. E_i' was observed to decrease with increasing exposure time at 180°C for three of the four phenolic resins. The exception was the blend composite for which E_i' stayed roughly constant.

Effect of Thermal Exposure on E', Tan δ, and E''

Novolac/S-glass

Plots of E'' and tan δ versus E_i' for the novolac composite aged at 180°C for 0, 1, 2, 7, and 28 days are shown in Figure 5(a,b), respectively. The plot E'' versus T of the unaged sample had three peaks at 187, 246, and 309°C, while the plot of tan δ versus T for the unaged sample had peaks at 192 and 248°C. Multiple peaks in the DMA traces of novolac resins have been attributed to a low degree of cure of the molded resin.[14] Once the resin is heated through the glass transition, the cure continues. This results in an increase in crosslinking and, therefore, the glass transition temperature.

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Table I Effect of Thermal Exposure on Initial Storage Modulus of Phenolic Resins

Resin (Glass Type)	Initial Storage Moduli (E'_i) for Specimens Aged at 180 °C for Different Time Periods [GPa] (% of Initial Storage Modulus of Unaged Sample)				
	0 Days	1 Day	2 Days	7 Days	28 Days
Resol (S)	17.0 (100)	16.7 (98)	15.5 (91)	12.9 (76)	11.6 (68)
Novolac (S)	30.5 (100)	29.5 (97)	25.2 (83)	16.8 (55)	16.7 (55)
Blend (S)	20.5 (100)	20.2 (99)	18.1 (88)	18.8 (92)	19.5 (95)
Copolymer (S)	24.1 (100)	24.1 (100)	21.8 (90)	20.7 (86)	17.4 (90)

Following thermal aging, the plots of E'' and tan δ versus T changed significantly. The magnitudes of E'' and tan δ for the aged samples were reduced compared to the unaged sample. For instance, the maximum value of E'' for the aged samples was 0.6 GPa at 350°C for the sample aged 1 day, while the maximum value of E'' for the unaged sample was approximately 1.9 GPa at 187°C. Furthermore, the maximum value of E'' and tan δ decreased as the aging time was increased from 1 to 2 to 7 to 28 days.

Plots of E' versus T for the novolac/S-glass composite following aging at 180°C for 0, 1, 7, and 28 days are shown in Figure 5(c). Although the initial (40°C) storage modulus decreased with aging time at 180°C, at higher temperatures, the E' for the aged composites were larger than was the E' for the unaged composite. The increase in E' at higher temperatures following thermal aging at 180°C for 1 day is indicative of the continuing (post)cure of the novolac resin. Decreases in the magnitude of E'' and tan δ are also consistent with the cure of the resin portion of the composite.

E' decreased, at a given temperature, with aging time at 180°C. This may be indicative of thermal degradation of the resin or degradation of bonding at the fiber–resin interface.

Resol/S-glass

Plots of E'' and tan δ versus T for the resol/S-glass composite aged at 180°C for 0, 1, and 28 days are shown in Figures 6(a,b), respectively. The unaged composite had two peaks in the tan δ versus T plot at approximately 214 and 250°C.

Thermal aging led to a decrease in the magnitude of E''. There were shoulders in the plot of E'' versus T at approximately 150 and 300°C for the sample aged 1 day, while E'' increased monotonically with temperature for the sample aged 28 days. The magnitude of E'' at a given temperature decreased as aging time increased. Although tan δ decreased following thermal aging, the magnitude of tan δ for the sample aged 28 days was larger than that for the sample aged 1 day at temperatures above 160°C. A number of spikes were seen on the plots of E' and tan δ versus T for the sample aged 28 days. These could be due to changes in the geometry of the sample, changes in the internal stress of the sample induced by the heating of the sample, or indicative of degradation of the bond between the resin and the reinforcing fiber resulting in fiber slippage. The decrease in the magnitude of E'' and tan δ with aging time is consistent with the cure of the resol resin.

Resol–Novolac Blend/S-glass

Plots of tan δ and E'' versus T for the resol–novolac blend/S-glass composite following aging at 180°C for 0, 1, 2, 7, and 28 days are shown in Figure 7(a,b). The unaged samples had maxima in the plots of tan δ and E'' versus T at 178 and 172°C, respectively, which are characteristic of the glass transition of the blend. Both of the plots also had peaks at approximately 220, 275, and greater than 300°C. As was discussed for the novolac composite, the complicated response of the unaged blend composite has been attributed to the continuing cure of the resin as the temperature is increased through the glass transition.[14]

After thermal aging at 180°C for 1 day, the plots of E'' and tan δ versus T for the resol/novolac blend had a single peak at approximately 310°C. The magnitude of E'' and tan δ at a given temperature decreased relative to the unaged sample. The increase in the temperature of the maximum in the tan δ and E'' versus T and the decrease in the magnitude of E'' and tan δ are characteristic of an increase in crosslinking (cure). The temperature of the maximum in plots of E'' and tan δ versus T increased and the magnitude of E'' and

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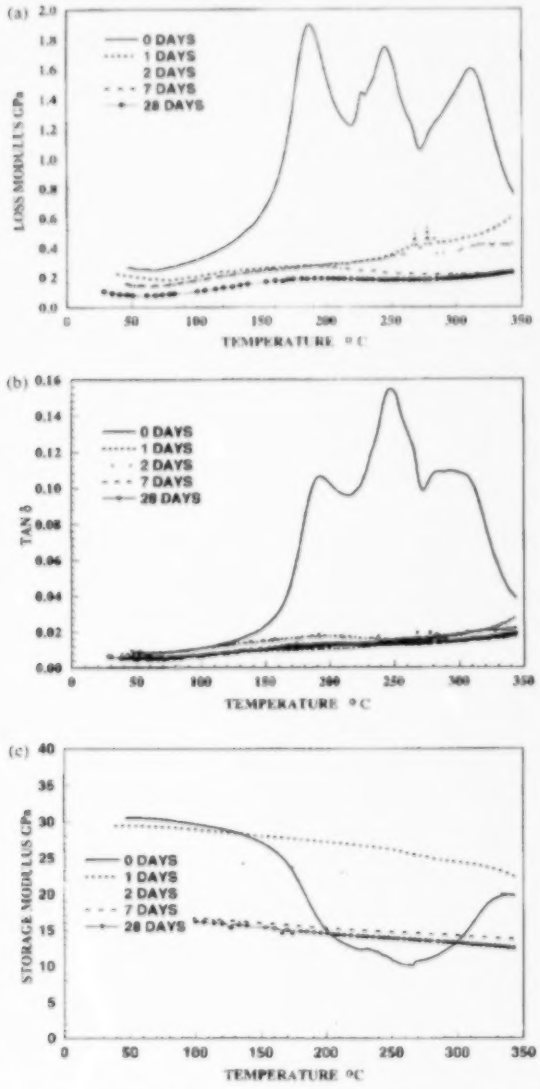

Figure 5 Development of cure in novolac/S-glass composite aged at 180°C for different lengths of time (as measured by DMTA): (a) loss modulus versus temperature; (b) tan δ versus temperature; (c) storage modulus versus temperature.

tan δ decreased as aging time was increased from 1 to 28 days.

Plots of E' versus T for the composites aged 0, 1, 2, 7, and 28 days are shown in Figure 7(c). The initial modulus (at 40°C) of this composite decreased slightly as aging time was increased from 1 to 2 to 7 days and then increased for the sample aged 28 days. At temperatures above 150°C, the magnitude of E' was much higher for the thermally aged samples. This is indicative of the more complete cure of the resin resulting from thermal aging. The decrease in E' for the samples aged 2, 7, and 28 days may be indicative of degradation of the resin or the fiber/resin interface.

Comparison of Figures 5, 6, and 7 indicates that the dynamic mechanical response of the resol/novolac blend composite following thermal aging was different from the dynamic mechanical response of either the resol or novolac resin composites. The dynamic response of the unaged blend most closely resembled that of the unaged novolac, although the T_g's and the positions of the other peaks in the tan δ and E'' versus T plots were different for the two samples. The blend had a maximum in the plot of E' versus T below 350°C, whereas the novolac and resol resin com-

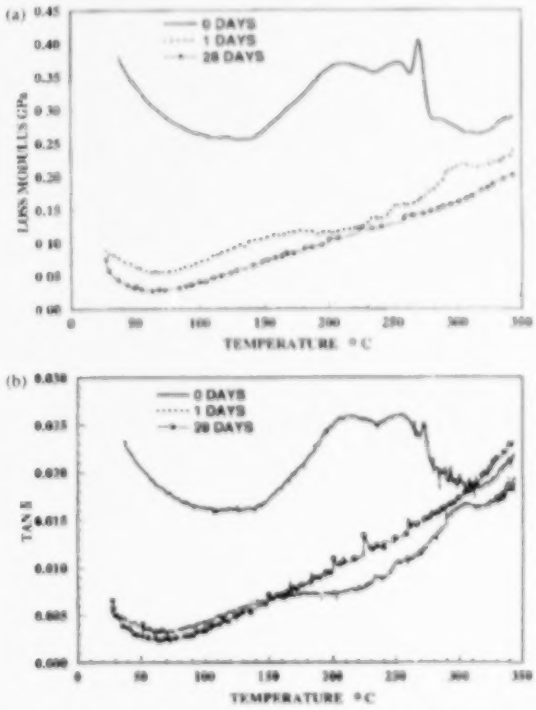

Figure 6 Development of cure in resol/S-glass composite aged at 180°C for different lengths of time (as measured by DMTA): (a) loss modulus versus temperature, (b) tan δ versus temperature; (c) storage modulus versus temperature.

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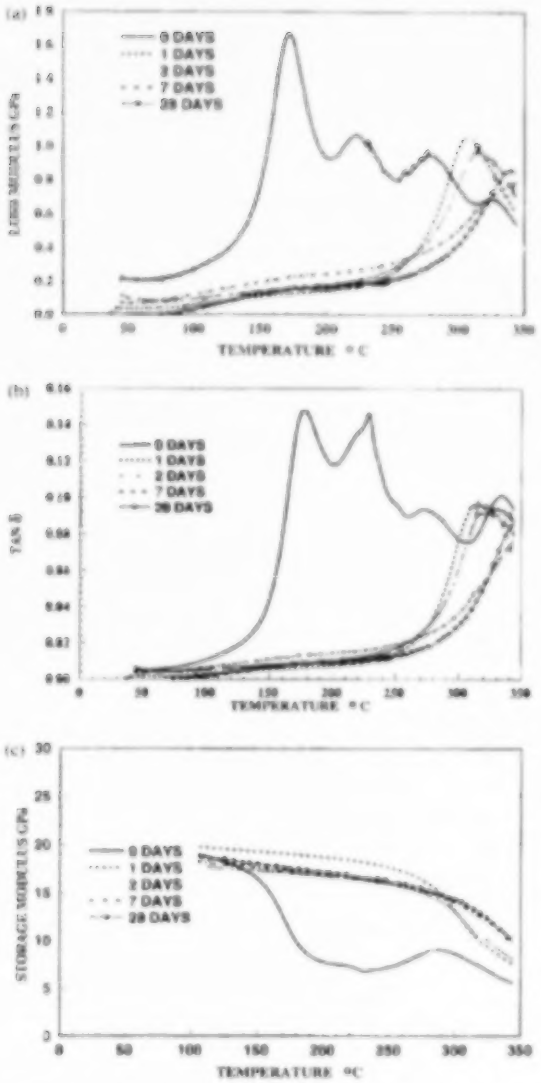

Figure 7 Development of cure in resol-novolac blend/S-glass composite aged at 180°C for different lengths of time (as measured by DMTA): (a) loss modulus versus temperature; (b) tan δ versus temperature; (c) storage modulus versus temperature.

posites did not exhibit a maximum in the plot of E' versus T at temperatures up to 350°C. Also, the aged blend had maximum E'' and tan δ values that were significantly higher than the maximum value for aged samples of either the novolac or the resol resin composites. These differences indicate that the structure of the resol/novolac blend composite is different from either the resol composite or the novolac composite.

Phenolic–Furan Novolac and Resol Graft Copolymer

Plots of E'' and tan δ versus T for the graft copolymer composite following aging at 180°C for 0, 1, 2, 7, and 28 days are shown in Figure 8(a,b), respectively. The plot of E'' for the unaged sample had a maximum at approximately 150°C, while the plot of tan δ versus T had a maximum at approximately 210°C with a shoulder at 155°C. Thermal aging led to a decrease in the magnitude of E'' and tan δ, although the decrease did not correlate with aging time, that is, the plots of E'' and tan δ versus T for the sample aged 7 days had maxima greater than those for the samples aged 1 and 2 days. This is in contrast to the other composites where the magnitude of the maxima of E'' and tan δ decreased with aging time.

The increase might be due to the opening of the furan ring in the novolac furan phenolic portion of the resin. This would act to allow more motion of molecular fragments and counteract the reduction in the motion resulting from increased crosslinking in the thermally aged composites. The magnitudes of E'' and tan δ were lowest for the sample aged 28 days.

The effect of thermal aging on the dynamic mechanical response of the copolymer composites was similar to that for the resol/novolac blend composites, that is, aging resulted in a decrease in the magnitude of E'' and tan δ and an increase in the temperature where these parameters had their highest values (approximately 300°C). The existence of peaks in these plots is in contrast to the plots for the resol and novolac composites, and the magnitude of E'' and tan δ is greater than that found for the resol and novolac resins.

The plots of E' versus T for the copolymer composite aged 0, 1, 2, 7, and 28 days at 180°C are shown in Figure 8(c). Thermal aging for 1 day had no effect on the initial modulus of this composite. However, the initial modulus decreased monotonically with further aging time. As was observed for the blend, the magnitudes of E' for the thermally aged composites were greater than for the unaged composite at temperatures above 100°C (1 day) and 150°C (28 days).

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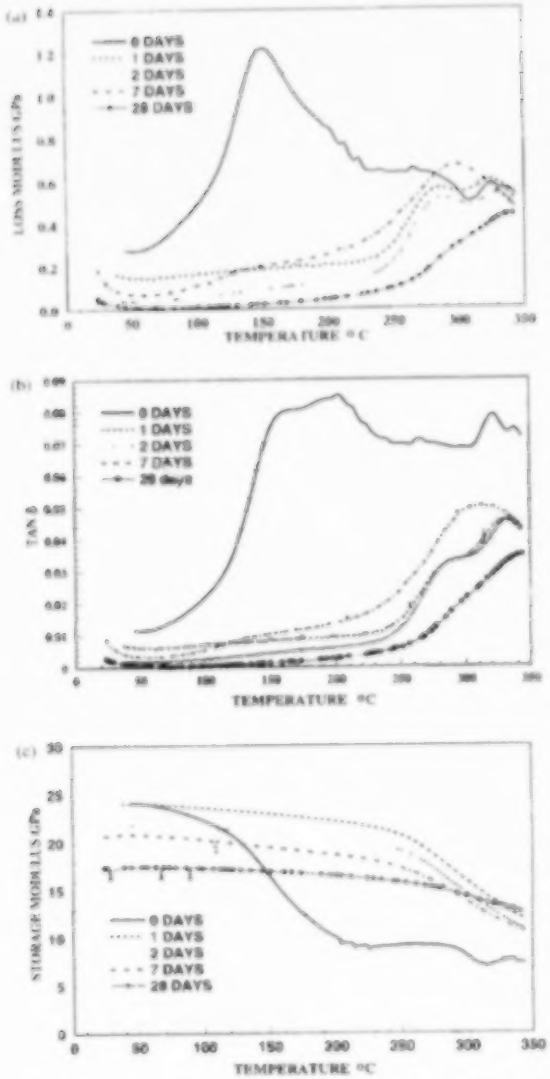

Figure 8 Development of cure in furan-based copolymer/S-glass composite aged at 180°C for different lengths of time (as measured by DMTA): (a) loss modulus versus temperature; (b) tan δ versus temperature; (c) storage modulus versus temperature.

CONCLUSIONS

DMA was used to study changes in the dynamic response (E', E'', and tan δ) of four phenolic composites following thermal aging at 180°C. The analyses indicated that the maximum values of E'' and tan δ decreased for each of the four composites following thermal aging at 180°C for 1 day. The initial magnitudes of E' (40°C) of the four composites following 1 day at 180°C remained unchanged but were larger than that of the unaged sample at higher temperatures. The decrease in the magnitudes of E' and tan δ and the increase in the magnitude of E' at higher temperatures are consistent with a more complete cure of the phenolic resins used in the composites.

Further aging of the composites led to a decrease in E', although the novolac and resol phenolics lost a greater percentage of their initial storage modulus than did the blend or copolymer composites after 28 days at 180°C. The decrease in E' with aging time indicates that the phenolic composites are degrading. Degradation of the resin and degradation of the bond at the fiber–resin interface are possible mechanisms and it is likely that both are responsible for the decrease in E'.

The dynamic mechanical responses of the resol and novolac composites were different from the blend and copolymer composites and the differences persisted with increasing aging time. The blend and copolymer composites had higher E'' and tan δ values than those of the resol and novolac composites and distinct maxima in the plots of E'' and tan δ versus T. The difference in the response indicates that the structure of phenolic composites can be altered by using blended or copolymer resins. Studies on the effect of thermal aging on "neat" resin samples are planned. The results of these studies will be used to discuss the relative effect of resin and fiber/resin interfacial changes on the dynamic response of the phenolic composites.

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